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CHEMICAL LASER SYSTEMS

Milton J. Linevsky, et al

General Electric Company

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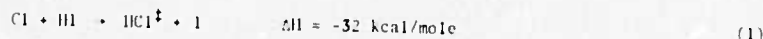
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13. ABSTRACT

A number of chemical reactions leading to the formation of vibrationally excited HCl have been studied spectroscopically employing a diagnostic technique developed during the earlier course of this program. To date the most promising system examined is the exchange reaction:



Chlorine atoms were produced by microwave discharge in chlorine-helium mixtures and rapidly mixed with HI in a fast-flow reactor at a pressure of approximately 3 torr. Under these conditions, 3 watts (cw) of laser power have been obtained in a number of P-branch vibrational-rotational transitions in HCl. Spectroscopic measurements of the total HCl population produced by the reaction indicate that, assuming no chaining, i.e., one HCl molecule produced per Cl atom introduced into the flow, approximately 20% of the Cl<sub>2</sub> is dissociated to Cl atoms in the microwave discharge. Based on the energy released by (1) and the flow rate of Cl atoms, the estimated chemical efficiency has been found to be ca. 15%. Under these conditions, lasing lines from both HCl isotopes (HCl<sup>35</sup> and HCl<sup>37</sup>) have been observed.

An infrared interferometric technique has been employed to develop a diagnostic procedure which makes possible the spatial (time) measurement of the spontaneous HCl<sup>\*</sup> emission as a function of location along the flow axis of the reactor tube. During this reporting period, a fairly extensive effort has been made to improve the quality of the interferometrically derived line intensity data. Full implementation of this technique will considerably simplify the diagnosis of HCl lasers and should be applicable to the study of other lasing molecules as well, e.g., DF, HF, etc.

During the course of the studies on the Cl + HI reaction, measurements were made of the atomic iodine (<sup>2</sup>P<sub>1/2</sub>) + (<sup>2</sup>F<sub>3/2</sub>) emission which has been observed to accompany that from HCl. Because of the interest in iodine as a lasing species, a brief study of the source of this emission in the Cl + HI reaction and in the [O(<sup>3</sup>P), O<sub>2</sub>(<sup>1</sup>Δ, <sup>3</sup>Σ)] + HI reaction have been carried out.

A number of other HCl producing reactions have also been studied; a spectroscopic examination of the SO + N<sub>2</sub>O reaction to produce SO<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) has been initiated and some additional work on the CS<sub>2</sub>/N<sub>2</sub>O/O<sub>2</sub> flame laser has been carried out. However, since this work is not yet complete, the results will not be included in this report but will be discussed thoroughly in the Final Report.

Finally, a small effort to investigate means for efficiently producing metal atoms by chemical reaction has been initiated. In these experiments, Cu metal atoms were electrically excited by means of a pulsed electric discharge through CuCl vapor diluted with Argon. In a separate set of experiments, the CuCl/Ar mixture was reacted with Na, viz.,



Spectroscopic measurements of the copper 3248Å and 5105Å emission lines showed that the addition of Na enhances radiation trapping in the 3248Å resonance transition suggesting that reaction (2) substantially increases the Cu atom concentration in the discharge gases.

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CHEMICAL LASER SYSTEMS

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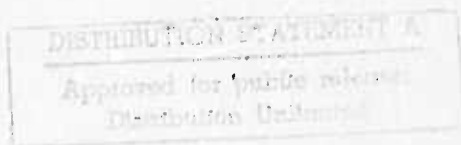
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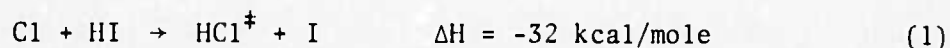
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## SUMMARY

A number of chemical reactions leading to the formation of vibrationally excited HCl have been studied spectroscopically employing a diagnostic technique developed during the earlier course of this program. To date the most promising system examined is the exchange reaction:



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As has already been described in Ref. (1), an infrared interferometric technique has been employed to develop a diagnostic procedure which makes possible the spatial (time) measurement of the spontaneous  $\text{HCl}^{\dagger}$  emission as a function of location along the flow axis of the reactor tube. During this reporting period, a fairly extensive effort has been made to improve the quality of the interferometrically derived line intensity data. Full implementation of this technique will considerably simplify the diag-

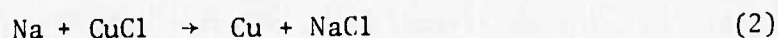


nosis of HCl lasers and should be applicable to the study of other lasing molecules as well, e.g., DF, HF, etc.

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A number of other HCl producing reactions have also been studied; a spectroscopic examination of the  $SO + N_2O$  reaction to produce  $SO_2(^3B_1)$  has been initiated and some additional work on the  $CS_2/N_2O/O_2$  flame laser has been carried out. However, since this work is not yet complete, the results will not be included in this report but will be discussed thoroughly in the Final Report.

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## 1.0 INTRODUCTION

Part of the work performed under the present contract represents a continuation of last year's program. In that effort, a large number of combustion systems were examined spectroscopically to determine whether, under certain conditions, population inversions are produced in reaction products. The systems were examined in two separate experimental facilities: a conventional variable pressure flame apparatus; and a fast-flow reactor constructed during the course of the program. As a result of this work it was found that several carbon containing fuels, namely, cyanogen, acetylene, and carbon bisulfide, led to the production of highly vibrationally excited CO when reacted with atomic and/or molecular oxygen at reduced pressures (1-100 torr).

On the basis of these results it was proposed that studies of the  $\text{CS}_2/\text{O}_2/\text{N}_2\text{O}$  system be extended. In addition to the continuing effort on CO, a screening program to investigate HCl producing reactions was proposed. In this work, a number of combustion systems which can potentially lead to vibrationally excited HCl were to be examined both in the flow reactor and in the low pressure flame facility. Also proposed for investigation under the current contract was the possibility of obtaining visible chemical lasing from species such as metal oxides. Specifically, metals derived from metal carbonyls or alkyls were to be interacted with atomic/molecular oxygen, or in some cases with  $\text{N}_2\text{O}$ .

Some phases of the above work have been carried out and reported on in the Semi-Annual Technical Report on Chemical Laser Systems (Ref. 1) which describes the work performed on the present contract during the time period March 1, 1973 to September 1, 1973. This Interim Report describes



the work carried out in the time period September 1, 1973 to February 28, 1974, and details of the earlier work will not be repeated herein.

During this reporting period, the bulk of the effort was spent on studying the  $\text{Cl} + \text{HI}$  reaction which has been found to be quite efficient in its production of  $\text{HCl}^\ddagger$ . A small effort has also been directed to the excitation of atomic iodine formed in the  $\text{Cl} + \text{HI}$  and in the  $\text{O}/\text{O}_2(^3\Sigma, ^1\Delta)/\text{HI}$  reactions.

Finally, a relatively modest effort was to be devoted to the study of "chemical/electrical hybrid lasers". Included for investigation in this category were means for chemically producing species in which population inversion could be induced electrically. The work to be reported on the copper vapor generator represents a preliminary effort toward this objective.

## 2.0 HCl STUDIES

### 2.1 BACKGROUND

The practical incentive for the study of  $\text{HCl}^\dagger$  producing reactions stems from the need to produce an efficient high power laser system operating at wavelengths lying within an atmospheric window. The HCl molecule with vibrational-rotational transitions in the wavelength region  $3.7\text{-}4.0\mu$  seems especially attractive in this regard. For example, Wang (Ref. 2) has recently computed the atmospheric transmission for a number of  $v = 3 \rightarrow 2$  and  $v = 2 \rightarrow 1$  P-branch transitions of  $\text{HCl}^{35}$  and  $\text{HCl}^{37}$ . Included in the model were atmospheric attenuation by  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  as well as extinction by aerosols. The results show that the vertical transmittance through the entire atmosphere for the  $J = 8 \rightarrow 4$  lines are about 90% or greater; the horizontal transmittance of these lines for a 10km path length at sea level are about 70% or greater.

Although HCl was the first molecule in which chemical pumping was observed, it seems that until recently relatively little effort has been directed toward the development of a chemical laser based on this molecule.

Much of the fundamental work on  $\text{HCl}^\dagger$  producing reactions has been carried out by Polanyi and his colleagues (Refs. 3-5) over the past six years. In these experiments, measurements of the spontaneous emission from  $\text{HCl}^\dagger$  at very low pressure have permitted a determination of the relative rates at which a given chemical reaction populates the individual levels of the product molecule. A compilation of some pertinent reactions for which such information is available is given in Table I. The table lists the frac-

TABLE I

## FUNDAMENTAL MEASUREMENTS ON SOME HCL PRODUCING REACTIONS

REACTION	EXOTHER- MICITY kcal/mole	$f_T$	$f_V$	$f_R$	$k_0$	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$	$k_6$
H + Cl <sub>2</sub> → HCl + Cl	46.5	0.49	.43	.08	~ 0	0.2	0.7	1.0	0.1	---	---
Cl + HI → HCl + I	32.0	0.16	0.71	0.13	~ 0	0.2	0.3	1.0	0.7	---	---
Cl + DI → DCl + I	32.0	0.16	0.71	0.13	0	0.12	0.35	0.73	1.0	0.05	
D + Cl <sub>2</sub> → DCl + I	46.5	0.49	0.40	0.10	0.1	0.33	1.0	0.86	0.25	0.06	
H + SCl <sub>2</sub> → HCl + SCl	46.0		0.43		0.3	0.53	0.72	1.0	0.83	0.25	
F + D <sub>2</sub> → DF + F	34.5	0.27	0.66	0.07	~ 0	0.7	1.0	0.7			

$f_{T,V,R}$  = Fraction of Energy in Translation, Vibration, Rotation.

$k_n$  = Relative Rate Constant for Population of  $n^{\text{th}}$  Vibrational Level.

tion of the exothermicity that appears in the three degrees of freedom of the product, and the relative rates at which the vibrational levels are populated. For all of the reactions listed, the vibrational levels of the products are populated up to the limit determined by the exothermicity of the reaction. Data for DF has been included for comparison because, as for HCl, DF vibrational-rotational transitions lie in a very favorable wavelength region.

The data in Table 1 show, for example, that the Cl + HI reaction compares favorably with F + D<sub>2</sub> with respect to both the energy released and the mode in which the reaction partitions energy into accessible vibrational levels. In the evaluation of this reaction as a pumping source for a high power laser, the absolute values of the rate constants for HCl<sup>‡</sup> formation and quenching must be taken into account, as well as other practical considerations such as the high atomic weight of iodine which may increase system weight and make diffusive mixing of Cl with HI difficult. However, proper injector design and the possibility of recycling the iodine to make HI may minimize these problems and should be the subjects of investigation in future work.

## 2.2 FLOW REACTOR STUDIES

### 2.2.1 Flow Reactor and Optical Set-Up

A schematic of the flow reactor employed in these studies is shown in Figure 1. The device was constructed in sections to permit disassembly for cleaning or for modification. Diluent gas, He, Ar, etc., is admitted into the first section, allowed to expand, and is then injected downstream through a perforated plate to obtain uniform flow throughout the reactor

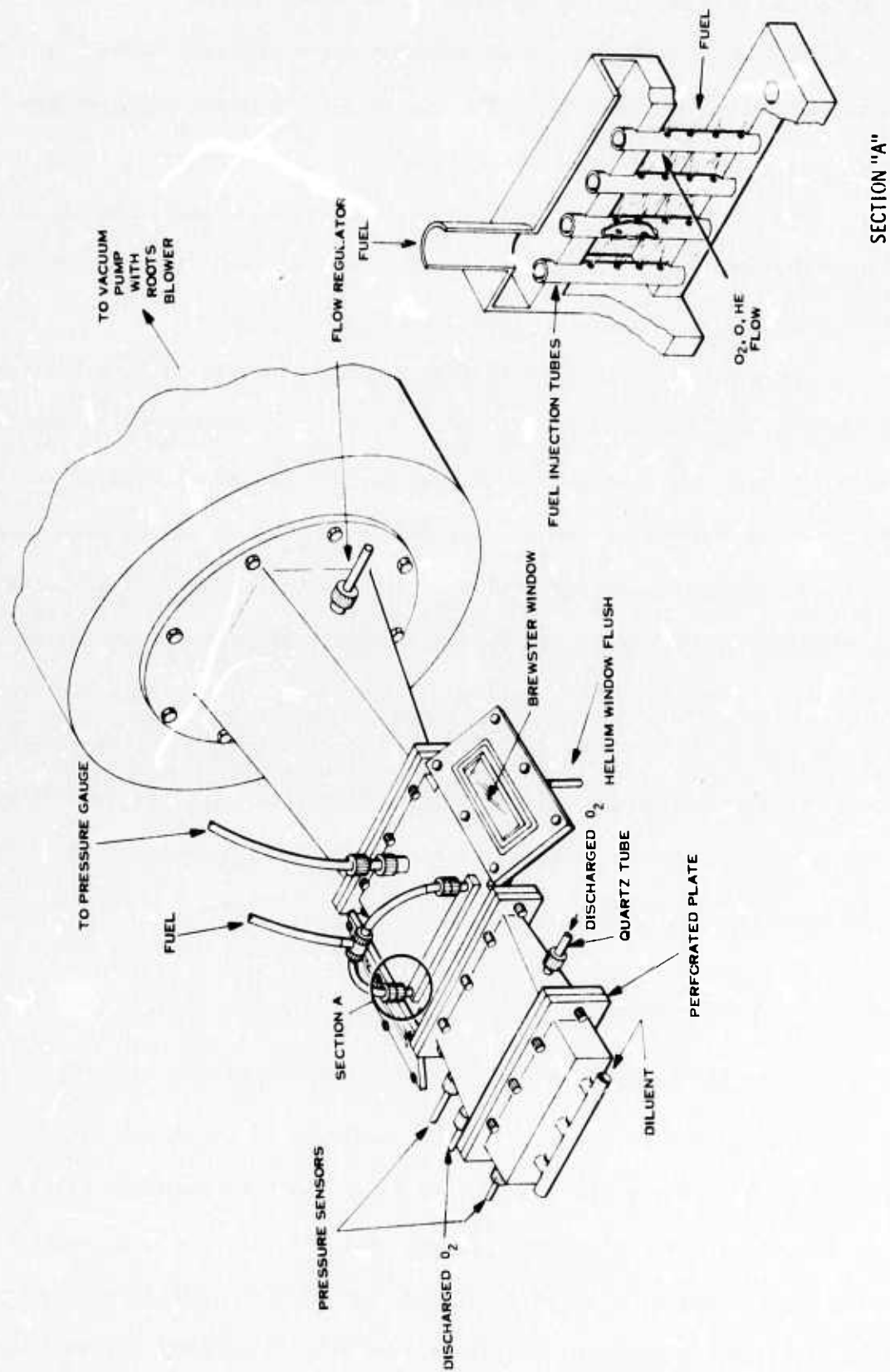


Figure 1. Flow Reactor Schematic

cross-section. Discharge products are admitted into the second section via a 0.5" diameter quartz tube which traverses the 6" reactor width. The gases are injected downstream through a number of holes drilled along the length of the tube. Half of the total discharge flow enters through each end of the quartz tube; two microwave (2450 MHz) power supplies, each rated at 125 watts are used as power sources, and energy is coupled into the gases in nitrogen-cooled Evanson cavities. The reactor sections through which the discharges flow are lined with teflon tape to minimize surface recombination of atoms.

Fuels are injected into the laser section, in a direction perpendicular to the main gas flow, through a total of approximately 15 holes drilled into the injector tubes (see section "A", Figure 1). The 7" long laser section is fitted with rectangular Brewster salt windows so that optical measurements can be made in the volume of gas extending from the injector tubes to a point 4" downstream. A small flow of inert gas is uniformly distributed over the window surface to help keep them clean. Cavity mirrors are mounted on an optical bench and can be translated along the direction of gas flow. Gases from the laser section exit through an expansion section into a plenum chamber and are exhausted with a 1200 cfm Roots blower.

Measurements of spontaneous emission were made along the length of the flow reactor. For this purpose, a light gatherer consisting of a number of mirrors and stops was employed to obtain a spatial resolution of approximately 2 mm along the direction of gas flow. For typical flow conditions, this corresponds to a time resolution of  $\sim 15$  microseconds. Spectroscopic measurements of the lasing lines and of the spontaneous HCl emission were made with a Digilab FTS-14 scanning interferometer using  $\text{LN}_2$  cooled Hg:Cd:Te



or PbS detectors.

## 2.2.2 Cl + HI Reaction

### 2.2.2.1 Measurements of Lasing Power

As discussed in the Semi-Annual Report (Ref. 1) the primary objective of the work on this reaction was to develop an optical diagnostic technique to facilitate the study of reaction systems which may lead to efficient HCl lasing. It was felt that through a detailed analysis of the spontaneous HCl emission, the performance of a number of  $\text{HCl}^\dagger$  producing reactions could be rapidly evaluated. The Cl + HI reaction was chosen as the basis for this study as a matter of convenience because this system was found to produce HCl lasing quite easily, i.e., lasing action could be observed over a broad range of pressure and stoichiometry. As time went on, however, and as experience was gained with other HCl producing systems, it was soon realized that the Cl/HI reaction was more promising than originally anticipated. As a result, a substantial effort has been expended on the study of this system.

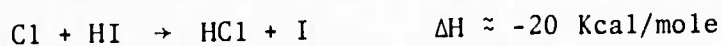
To date approximately 3.2 watts of lasing power has been obtained from a  $\text{Cl}_2/\text{HI}/\text{He}$  mixture having a molar ratio of 1/1.66/125 at a total pressure of 3.7 torr; the same power level was obtained from a  $\text{Cl}_2/\text{HI}/\text{Ar}$  mixture having a molar ratio of 1/1.66/31 at 1 torr. In both experiments, the flow of  $\text{Cl}_2$  was 0.44 millimoles per second, the average gas velocity was about 140 meters per second, and the output was coupled from the cavity through a 3% transmitting dielectrically coated mirror. The total output obtained using two 3% mirrors, one on each end of the cavity, was virtually identical (1.55 watts/mirror) to that obtained using a single mirror; on this basis, optimum coupling is estimated to be between 3 and 6%. With a 3% coupling

mirror and a KBr flat placed intracavity to introduce an approximately 6% scattering loss, lasing was quenched. It is therefore estimated that neglecting absorptive and mirror (2%?) losses, the small-signal-gain in the system lies between 6 and 9% per round trip ( $\sim 30$  cm) pass.

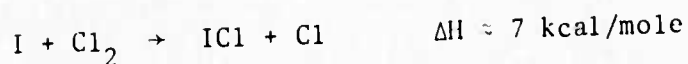
In the experiments described, the HI flow rate was about 0.75 millimoles per second. If it is assumed that laser output is limited by the HI flow, then, based on the exothermicity of Reaction (1) and the flow rate of HI, the maximum cw power level which can be achieved is ca. 98 watts. On this basis, the observed power level of 3.2 watts implies a minimum value of about 3.3% for the chemical efficiency.

In the preceeding calculation of efficiency, it has been tacitly assumed that approximately 83% or more of the  $\text{Cl}_2$  flow is converted to Cl atoms, viz.,  $0.44 \text{ millimoles/sec} \times 0.83 \times 2 = 0.73 \text{ millimoles/sec} = \text{HI flow rate}$ . As has already been discussed in the Semi-Annual Report (Ref. 1), based on spectroscopic measurements of the total HCl concentration, a maximum of about 20% of the total  $\text{Cl}_2$  flow is converted to Cl atoms which ultimately form HCl via Reaction (1). On this basis, the laser output is limited by the Cl atoms produced in the flow; the maximum power levels which can be achieved is about 23 watts and the observed output represents a chemical efficiency of 14%.

The dissociation of approximately 20% of the total  $\text{Cl}_2$  flow by microwave discharge seems anomalously high; however, such percentages have been reported in the literature (Ref. 6). An alternative explanation for the relatively high HCl yields is that additional Cl atoms are produced in the reactive flow. One possibility is the simple chain:

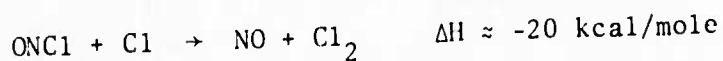


followed by



At the relatively low temperatures associated with the gas flow, the endothermic Cl producing reaction would be expected to be negligibly slow. Nevertheless, the possibility exists that part of the  $\text{Cl}_2$  emerging from the discharge is vibrationally excited and as a result the reaction of I with  $\text{Cl}_2$ , cannot positively be precluded at this time. No attempt has been made to spectroscopically measure ICl using either absorption or resonance fluorescence techniques.

Attempts have also been made to employ a variety of chlorine containing substances to produce Cl atoms in the electric discharge. The substitution of nitrosyl chloride (ONCl) for  $\text{Cl}_2$ , for example, was found to be reasonably effective. Approximately 1.1 watts of lasing power was obtained from an ONCl/HI/He mixture having the overall molar composition 1/3.5/260 at a total pressure of 3.6 torr. Based on the 0.21 millimole per second flow rate of ONCl, i.e., assuming 100% dissociation of ONCl to NO and Cl, the chemical efficiency is 4%. If it is assumed that 30% or so of the ONCl is dissociated in the discharge (the ON-Cl bond dissociation energy is approximately 38 kcal/mole vs 59 kcal/mole for  $\text{Cl}_2$ ), the chemical efficiency is about 13% - comparable to that obtained using the  $\text{Cl}_2$  discharge. Increasing the ONCl above the optimum value resulted in a decrease in power, suggesting quenching of  $\text{HCl}^\dagger$  by excess ONCl or a decrease in the Cl atom concentration by a reaction such as



or chain inhibition by the reaction



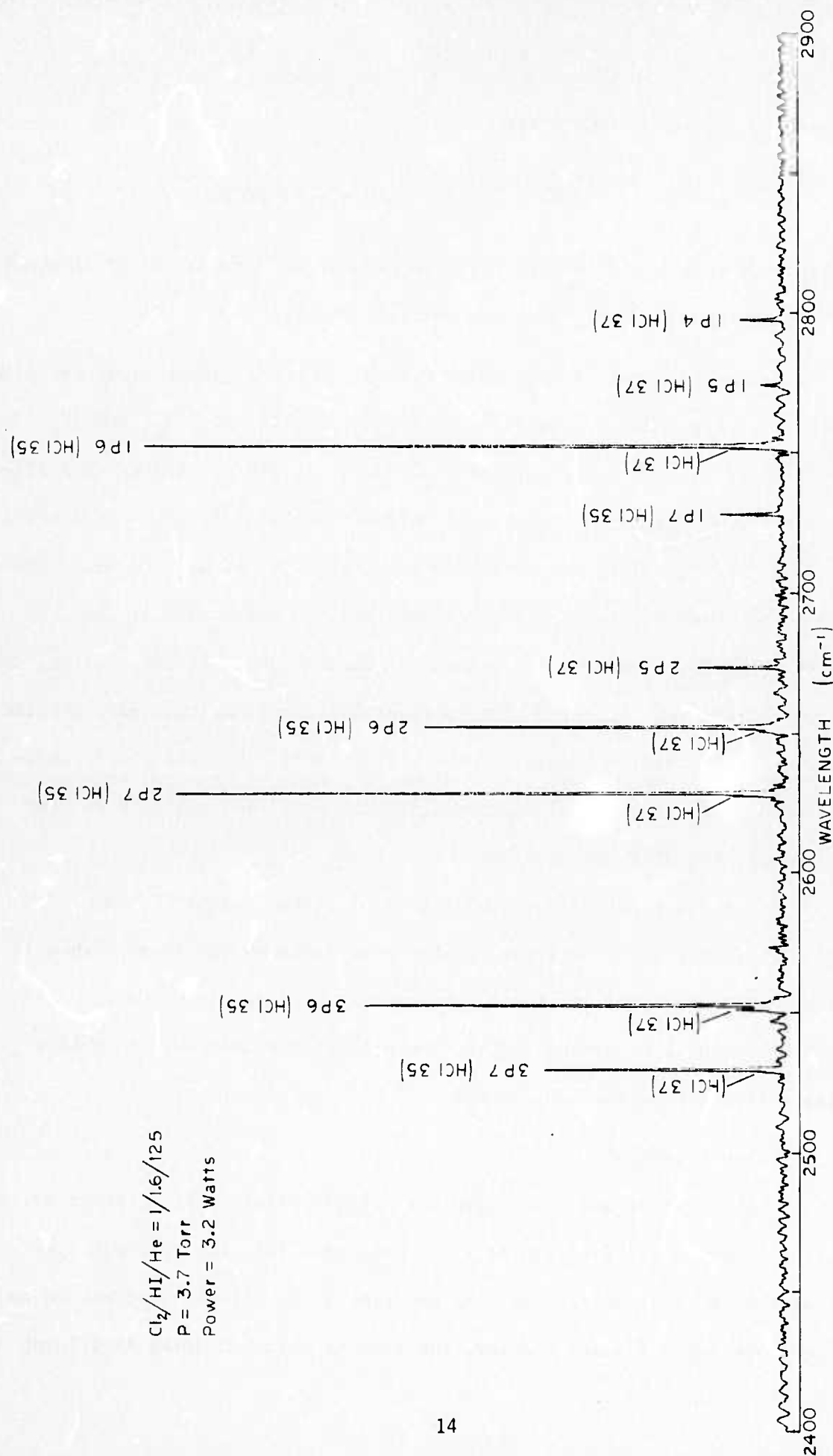
To date, the most suitable starting material for the production of Cl atoms in the microwave discharge has been found to be  $\text{Cl}_2$ .

The effect of several additives on the laser output power was also briefly investigated. The addition of Ar,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , NO,  $\text{CH}_4$ , and  $\text{SF}_6$  in quantities at least as large as the  $\text{Cl}_2$  flow rate, did not appreciably alter the power levels obtained with the  $\text{Cl}_2/\text{HI}/\text{He} = 1/1.66/125$ ,  $\text{Cl}_2 = 0.44$  millimoles/sec, mixture which was used as a baseline flow. It was, in fact, possible to maintain the same peak power level of 3.2 watts when Ar,  $\text{SF}_6$ , or  $\text{N}_2$  were substituted for He. In general, with the use of Ar,  $\text{SF}_6$ , or  $\text{N}_2$ , the peak power level was achieved with substantially lower diluent addition and at much reduced total pressures. With all diluents, the peak power conditions were found to occur at approximately the same flow velocity and for the same  $\text{Cl}_2$  (or HCl) concentration.

The addition of small quantities of either  $\text{N}_2\text{O}$  or  $\text{CO}_2$  was found to produce rather large decreases in the peak laser output level. This is, however, expected since it is well known that these molecules readily exchange vibrational energy with  $\text{HCl}^\dagger$ . No attempt has been made to obtain lasing action from either  $\text{CO}_2$  or  $\text{N}_2\text{O}$ .

#### 2.2.2.2 Spectroscopy

Shown in Figure 2 is a typical set of lasing lines obtained by reflecting a very small fraction of a 3.2 watt beam into the entrance aperture of the interferometer. In this experiment the diluent used was He and the pressure was 3.7 torr; however, the results obtained using Ar diluent at



$\text{Cl}_2/\text{HI}/\text{He} = 1/1.6/125$   
 $P = 3.7 \text{ Torr}$   
 Power = 3.2 Watts

Figure 2. HCl Lasing Line Spectrum

at lower pressure are similar. Note that in the nomenclature used to identify a transition,  $vP(J)$  or  $vR(J)$ ,  $v$  refers to the upper vibrational level while  $J$  refers to the lower rotational level of the transition. The isotopic abundance ratio  $Cl^{35}/Cl^{37}$  is approximately 3.08; therefore, assuming that the vibrational population distributions and the rotational temperature of  $HCl^{35}$  and  $HCl^{37}$  are identical, the gain in a given  $HCl^{35}$  transition should be about three times greater than that for a corresponding  $HCl^{37}$  transition. Under conditions of low gain the only lasing lines observed are those of the most abundant isotope. For the conditions shown in Figure 2, lasing transitions are observed for both isotopes. A peculiarity of these data is that for the  $HCl^{35}$  isotope, the strongest lasing transitions originate from the  $J = 6$  and  $5$  rotational levels of the upper vibrational levels, whereas for  $HCl^{37}$  the strongest transitions originate from the  $J = 4$  and  $3$  levels. Indeed, for the most intense  $HCl^{37}$  transition,  $2P(5)$ , the corresponding transition for  $HCl^{35}$  is not observed. Since, for a given vibrational level, the line of maximum gain is determined by the vibrational population ratio between the upper and lower levels and the effective rotational temperature, these data suggest significantly different population distributions and/or rotational temperatures for the two isotopes. Whether this effect is the result of cascading among the vibrational levels of the  $HCl^{35}$  isotope during lasing or vibrational exchange between  $HCl^{35}$  and  $HCl^{37}$  is uncertain.

Detailed, spatially resolved measurements of the  $HCl$  spontaneous emission have been carried out using a  $Cl_2/HI/Ar = 1/2.6/140$  mixture at a total pressure of 3 torr. The total flow of  $Cl_2$  in this experiment was about 0.12 millimoles per second. Typical spectra of the  $HCl$  spontaneous emission are shown in Figure 3. The data shown represent 20 co-added spectra of the



$\text{Cl}_2/\text{H}_2/\text{Ar} = 1/2.5/140$   
 $P = 3 \text{ Torr}$

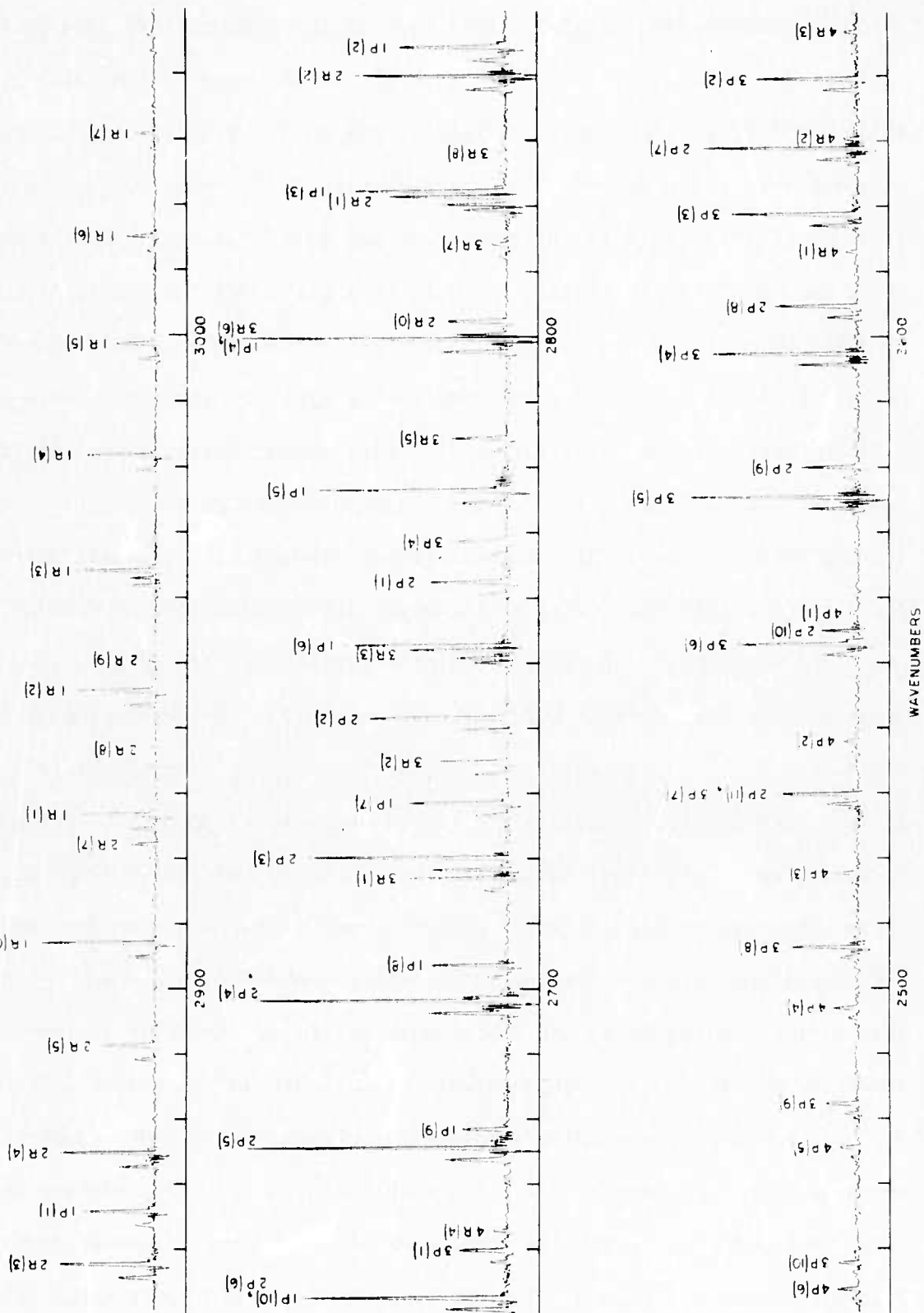


Figure 3. HCl Spontaneous Emission Spectra

HCl fundamental taken with  $0.5 \text{ cm}^{-1}$  spectral resolution. Associated with each transition are two peaks, the stronger from the  $\text{HCl}^{35}$  and the weaker from the  $\text{HCl}^{37}$  isotope. For a given transition in an optically thin gas, the  $I^{35}/I^{37}$  intensity ratio is 3.08 (Ref. 7).

As has already been discussed in Ref (1), the optically thin transitions could be employed directly to measure the rotational temperatures of the gas and to determine the vibrational population distribution of HCl relative to that in  $v = 1$  as a function of location in the flow reactor. In addition, it was found possible to employ those transitions which exhibit self-absorption ( $I^{35}/I^{37} < 3.08$ ), to measure the HCl concentration in the  $v = 0$  and  $v = 1$  vibrational levels. These data together with the relative population data permitted a total inventory of the HCl present at any location along the flow. From the results, it was possible to measure the small-signal-gain for several transitions which were observed to lase.

The spectroscopic data can also, in principle, be employed directly to identify transitions which have gain. Entirely analogous to the more generally encountered case in which emission lines are self-absorbed by the emitting medium, the intensity of a line originating from a transition between levels in which a population inversion exists will be augmented by stimulation emission. For HCl, optical gain can be identified for a given transition by inspection of the  $I_{\text{HCl}^{35}}/I_{\text{HCl}^{37}}$  isotopic intensity ratio. In this case, the small-signal-gain (negative absorption) of the more abundant isotope will always be greater than that for the less abundant isotope, and the resulting isotopic intensity ratio will exceed 3.08.

The use of isotopic intensity ratios for the measurement of gain is useful for several reasons. In the  $\text{Cl} + \text{HI}$  reaction, for example, the

rate constant for the production of HCl in the  $v = 0$  level is approximately zero (see Table I). Therefore, before appreciable quenching has occurred, the self-absorption of the  $v = 1 \rightarrow 0$  transitions will not be of sufficient magnitude to permit a determination of the HCl concentration in the  $v = 0$  level. Under these circumstances, the isotopic intensity ratios of the  $v = 1 \rightarrow 0$  transition provide a most convenient measure of gain. The method is also especially suited for use with the HCl<sup>35/37</sup> isotopes because, for a given transition, the isotopic line separation is less than 2 wavenumbers and corrections for system response with wavelengths are minimal. Also the formation kinetics and transition probabilities for the two isotopes can be considered to be identical.

As an example, examination of the data shown in Figure 3 shows that for several transitions, which are compiled in Table II, the observed isotopic intensity ratio exceeds 3.08. The lines for which this effect is observed are all P-branch transitions from rotational levels which are either the same or very close to those for which lasing action is observed. Under lasing conditions, the transitions having greatest gain are not necessarily identical to those which have the largest small-signal-gain because of cascading and other effects.

A plot of the expected variation of the isotopic ratios with the product  $\alpha_0 \ell$ , where  $\alpha_0$  is the small-signal-gain and  $\ell$  is the path length, is shown in Figure 4. The calculation was carried out using the classical "line-absorption" method of Ladenburg and Reike (Ref. 8) assuming Doppler broadened profiles for the HCl lines. A comparison of the isotopic ratio data given in Table II with the corresponding values of  $\alpha_0 \ell$  from Figure 4 shows that for most lines, especially the 2P(7) and the 1P(8) transitions,

TABLE II  
ISOTOPIC INTENSITY RATIO FOR LINES SHOWING GAIN

<u>TRANSITION</u>	<u>RATIO</u>	<u>TRANSITION</u>	<u>RATIO</u>
3P(6)	3.13	1P(8)	3.5
3P(5)	3.15	1P(7)	3.2
2P(7)	3.41	1P(6)	3.15
2P(5)	3.19		

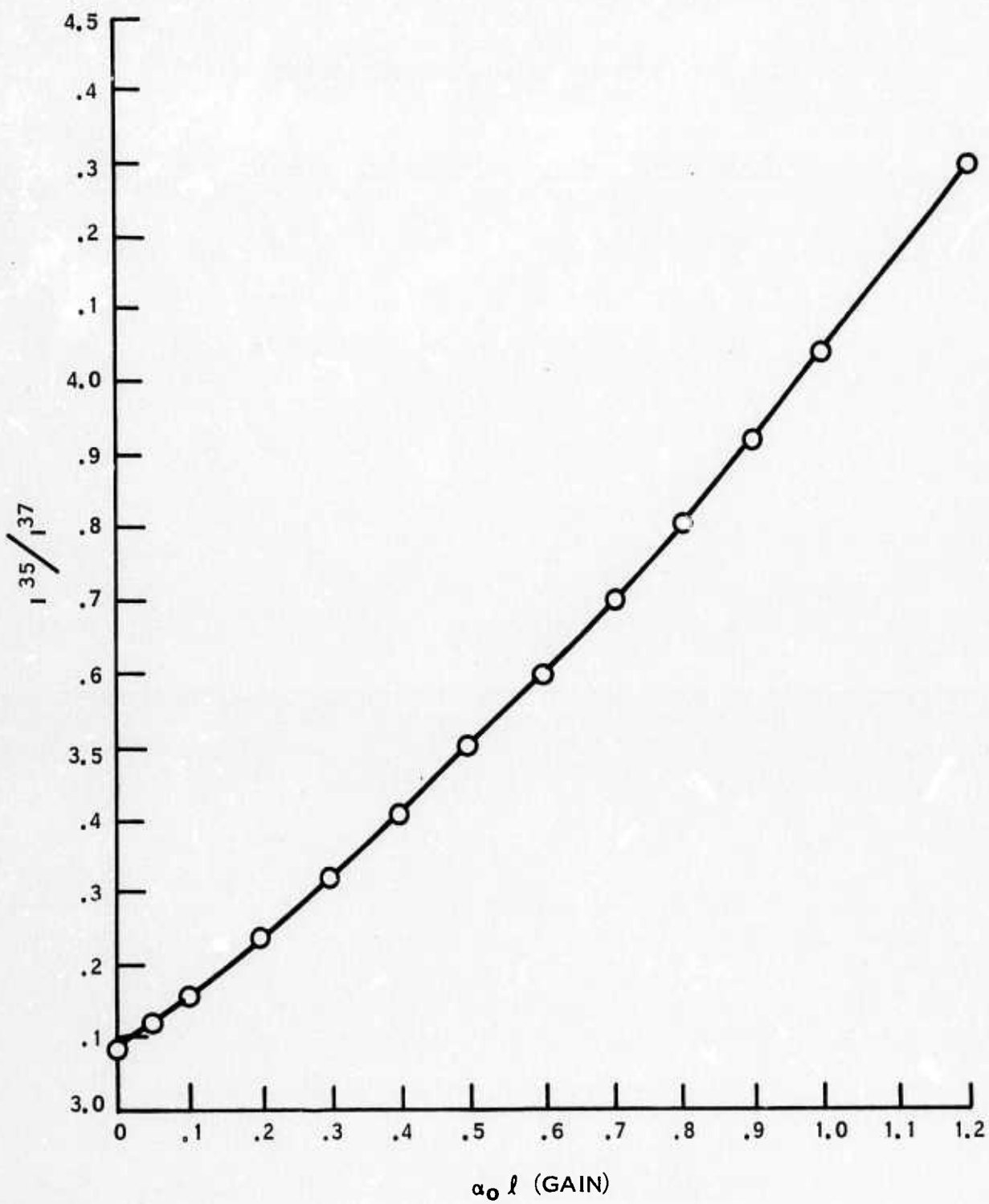


Figure 4. Isotopic Ratio vs Gain

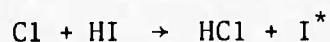
the values for gain obtained using this technique are unrealistically high. In fact, the principal limitation of this method seems to be the accuracy to which the line intensities could be measured.

A fairly extensive effort has been directed toward improving the accuracy of the intensity data provided by the infrared interferometer. A variety of techniques recommended by the manufacturer (Digilab) have been tried but to date intensity data reliable to better than about 10% have not been obtained and probably cannot be achieved employing the software package currently in the machine. However, a new software package which utilizes double-precision computational techniques has recently been made available and is scheduled for delivery in the very near future. It is felt that with this modification the accuracy of the interferometer will be much improved. Should this still not prove adequate, isotopic intensity ratios will be measured using a standard grating instrument with a suitable high sensitivity detector. Since, in this latter approach, the light collection efficiency of the interferometric method will be lost, it is felt that the small additional effort to be expended using the new computer software is warranted.

#### 2.2.2.3 Electronically Excited Iodine Production

Throughout the course of the Cl + HI studies in the flow reactor it has been observed that chemiluminescent iodine ( $^2P_{1/2}$ )  $\rightarrow$  ( $^2P_{3/2}$ ) emission accompanies the reaction. The emission commences at the Cl/HI mixing region and persists throughout the entire 10 cm length of the flow reactor.

There are two obvious mechanisms which can lead to hot iodine production. The first is the direct formation of  $I^*$  by:





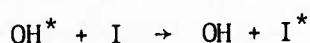
which is sufficiently exothermic to excite iodine; the second is vibrational transfer between ground state iodine and vibrationally excited HCl, viz.:



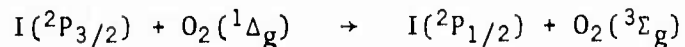
To help distinguish between those two mechanisms a series of experiments were carried out. It was found that very small flows of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  were sufficient to quench not only  $\text{HCl}^{\dagger}$  (as expected) but also  $\text{I}^*$  emission. In a related set of experiments, a flow of molecular oxygen and He was passed through the microwave cavities, and the mixture of atomic and molecular (ground state and  $^1\Delta_g$ ) oxygen produced was subsequently reacted with HI. In this experiment, it was found that for the same flow of HI as was used in the  $\text{Cl} + \text{HI}$  case, the  $\text{I}^*$  emission was approximately two orders of magnitude more intense. Furthermore, the addition of large quantities of  $\text{CO}_2$  or  $\text{N}_2\text{O}$  did not effect the intensity of the  $\text{I}^*$  emission.

Finally, atomic oxygen was produced by N atom titration with NO (i.e., little or no  $\text{O}_2(^1\Delta)$ ), and interacted with HI. In these experiments it was found that  $\text{I}^*$  emission intensity was comparable to that obtained in the  $\text{Cl} + \text{HI}$  reaction.

On the basis of these experiments, it has been tentatively concluded that in the  $\text{Cl} + \text{HI}$  reaction,  $\text{I}^*$  is excited by transfer with HCl in vibrational levels  $v \geq 3$ , and that a similar transfer mechanism, perhaps



gives rise to  $\text{I}^*$  in the  $\text{O} + \text{HI}$  reaction. The very strong emission observed in the  $\text{O}/\text{O}_2$  reaction with HI is very likely produced primarily by energy exchange of I with  $\text{O}_2(^1\Delta)$ , i.e.:



#### 2.2.2.4 Related Work

Within the last month of the reporting period several modifications have been made to the flow reactor and to the associated microwave discharge section. A new laser section has been constructed; similar in design to that shown in Figure 1, the new section incorporates a flat rectangular transparent lexan window in its upper surface. With this port, the flow within the reactor can be visualized at a variety of flow conditions (illumination provided by chemiluminescent reactions) to ensure proper mixing of fuel and oxidizer, etc. Plans are also being made to install a row of pin electrodes into the lexan top so that species formed by chemical reaction can be excited electrically. With regard to the discharge section, a 1000 watt, 2450 MHz, microwave power supply has been installed for discharging  $\text{O}_2$ ,  $\text{Cl}_2$ , etc.

### 3.0 VISIBLE CHEMICAL LASERS

#### 3.1 BACKGROUND

Chemiluminescent reactions which produce electronically excited species have received considerable attention as possible sources for pumping visible chemical lasers. Of special interest are metal oxide species which can be relatively easily formed in electronically excited states by chemical reaction, and for which, in some instances, favorable Franck-Condon factors exist for transitions from low vibrational levels of the excited state to high (non-thermally populated) vibrational levels of the lower electronic state. It has recently been reported (Ref. 8), for example, that in the reaction



electronically excited BaO ( $^1\Sigma^+$ ) is produced with an efficiency of approximately 10% (Ref. 9).

To obtain visible lasing between electronic transitions, a number of demanding criteria must be met. Depopulation of the upper laser levels by spontaneous emission, which can be almost ignored for infrared vibrational-rotational transitions, is an important loss mechanism in the visible region because of the large transition probabilities associated with electronic transitions. This loss, together with the fact that the pumping reaction will distribute its products among a number of rotational-vibrational levels in the upper state, imposes severe requirements for the pumping rate which must be achieved in order to produce threshold gain. Thus it has been esti-

mated (Ref 9) that to obtain visible chemical laser action in a diatomic molecule, excitation rates of the order of  $10^{19}$ - $10^{21}$  molecules/cm<sup>3</sup> sec are required. For excitation via a two-body reaction, for example, if it is assumed that the effective rate constant for pumping is ca.  $10^{-12}$  cm<sup>3</sup>/molecule second (i.e., ~1% efficiency for a gas kinetic reaction), then the product of the metal atom and oxidizer concentration which must be sustained for cw lasing must be quite high, of the order of  $10^{18}$ - $10^{22}$  molecule<sup>2</sup>/cm<sup>6</sup>. This result implies that to achieve chemical visible lasing, methods must be found to produce high flow rates of metals, and that the most promising reactions will involve oxidizers which can be supplied easily in relatively high concentrations, e.g., N<sub>2</sub>O, O<sub>2</sub>, etc.

In the work which has already been reported on in the Semi-Annual Report (Ref. 1), a number of chemical reactions have been investigated for their potential to produce electronically excited species, such as metal oxides, which may be of interest with regard to visible lasing. The approach taken was to spectroscopically survey the visible chemiluminescent emission produced by the interaction of metal or metal containing species with mixtures of atomic and molecular oxygen or with N<sub>2</sub>O. Following this survey, absolute intensity measurements of the band systems and continua were carried out and production rates for some excited species estimated. Although a number of reactions have been investigated in this manner, e.g., trimethylaluminum + O, BCl<sub>3</sub> + O, Ni (heated N<sub>1</sub>(CO)<sub>5</sub>) + N<sub>2</sub>O, Fe (heated Fe(CO)<sub>5</sub>) + N<sub>2</sub>O, the results obtained to date have not been encouraging in that, in all instances, only a very small fraction of fuel, ca.  $10^{-4}$ , could be converted to electronically excited oxide. Similar results have been obtained in a parallel study (Ref. 9) in which encapsulated metals were reacted with F<sub>2</sub>, N<sub>2</sub>O,

or  $O_2$ . On this basis, alternative methods were sought for easily producing metal atoms for either electrical excitation or for further reaction with an oxidizer to produce electronically excited diatomic metal compounds.

### 3.2 ALKALI METAL/METAL HALIDE STUDIES

A review of the physical properties of a number of metals and their compounds reveals that in several cases, the halides of relatively involatile metals can have appreciably high vapor pressures at just moderately elevated temperatures. Since in many cases the reaction of these halides with alkali metals, which are themselves relatively volatile, are exothermic and therefore conceivably fast, a small effort was initiated to determine whether the reduction of metal halides by, for example, Na, would be a favorable route for free metal production. The choice of the CuCl/Na system as the starting point for these studies was based on several factors. First, copper metal atoms are of inherent interest to the laser community; electrically pumped copper vapor lasers can potentially be quite efficient. Second, lasing action in Cu has been observed in electrically discharged CuCl vapor/diluent mixtures - the presence of CuCl does not therefore have a deleterious effect on the performance of the Cu laser. Finally, CuCl and Na are compatible in terms of temperature. For example, at 600°K the equilibrium concentration of Na (gas) over liquid sodium is  $\sim 6.4 \times 10^{14}/\text{cm}^3$  while the equilibrium concentration of  $(\text{CuCl})_3$  over CuCl (solid) is  $\sim 8.8 \times 10^{13}/\text{cm}^3$ . Therefore, at this relatively low temperature, both Na and Cu can be produced in roughly stoichiometric proportions and at sufficiently high number density to permit threshold conditions to be achieved for a reasonably small copper atom path length (note that to obtain  $\sim 2 \times 10^{14}/\text{cm}^3$  Cu (gas) over Cu (solid),  $T_{\text{eq}} \approx$

1600°K).

A schematic of the experimental apparatus is shown in Figure 5. The device consists, basically, of an instrumented quartz tube, resistively heated to temperatures of approximately 600-700°K. Electrical excitation was carried out by means of 5 kv, 1 KHz, pulses having risetimes of approximately 150 nanoseconds; the pulse width at half height was approximately 175 nanoseconds. When the experiments were initiated, a separately heated reservoir was used for vaporizing CuCl prior to its introduction into the tube. It was found, however, that CuCl could more easily and uniformly be distributed in the gas phase by simply allowing CuCl (solid), which was vacuum deposited on the walls of the quartz tube before the experiment, to vaporize as the tube was heated to its final temperature.

Measurements of the emission intensities of the Cu 5105Å green line and the 3248Å resonance line were carried out using a 1/2-meter JACO monochromator. In all experiments, Cu emission could only be observed while the discharge was turned on, i.e., no chemiluminescence could be observed in the reaction of  $(\text{CuCl})_3$  with Na.

At very low temperatures, i.e., low concentrations of  $(\text{CuCl})_3$  in the vapor phase, and with no sodium present, the intensity ratio,  $I_{3248\text{Å}}/I_{5105\text{Å}}$ , was approximately 100/1. As the temperature and therefore the concentration of  $(\text{CuCl})_3$  increased, radiation trapping of the resonance transition was observed; at  $T = 600^\circ\text{K}$ ,  $I_{3248\text{Å}}/I_{5105\text{Å}}$  was reduced to about 1/2.4. The introduction of Na into the tube under these conditions resulted in a five-fold increase in the intensity of the 5105Å line and a four-fold increase in the intensity of the resonance transition; the resulting  $I_{3248\text{Å}}/I_{5105\text{Å}}$  ratio therefore decreased to about 1/3. On the basis of these mea-



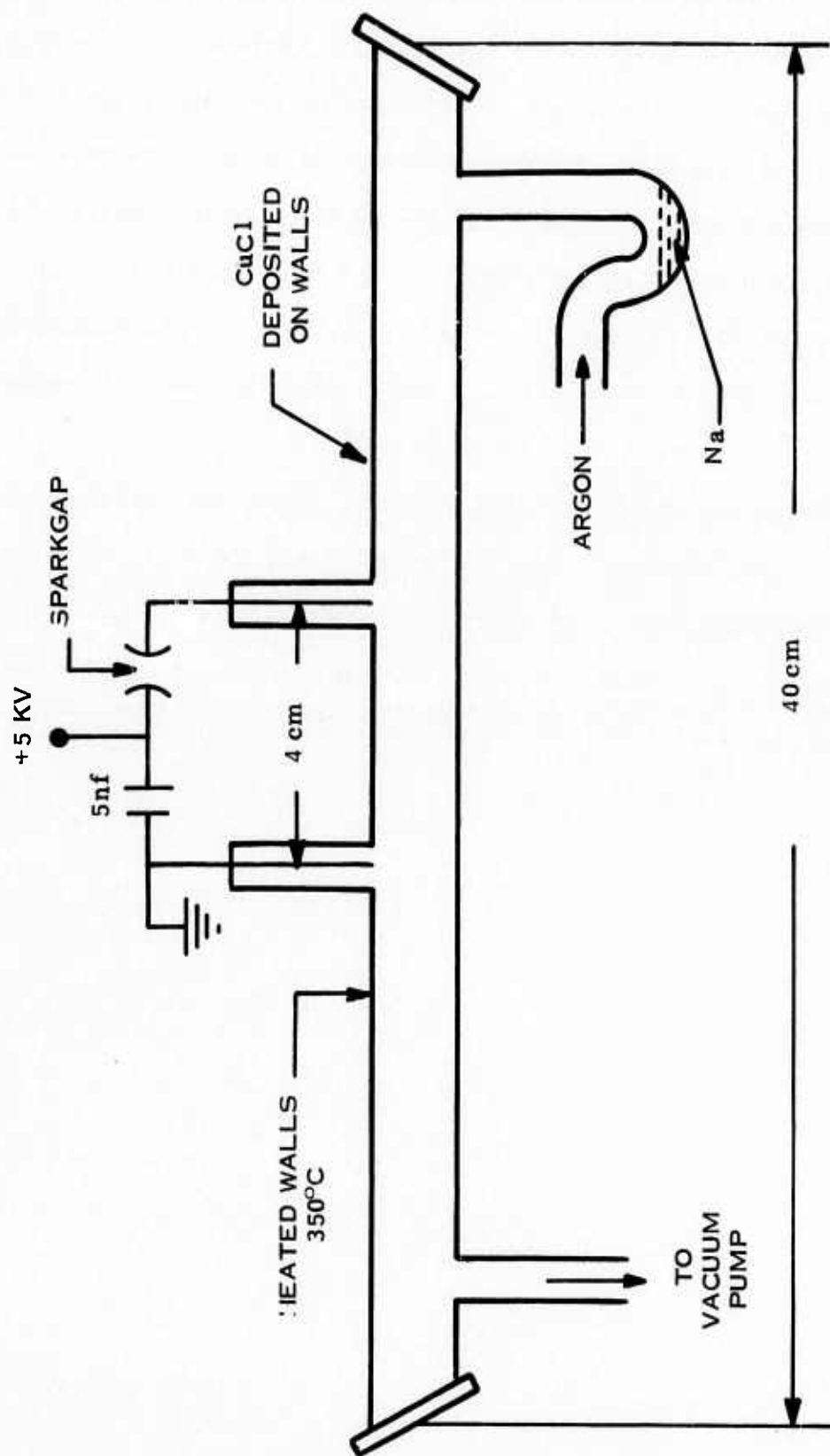


Figure 5. Metal Vapor Generator

surements, it was estimated that the copper atom concentration produced by the reaction of Na and  $(\text{CuCl})_3$  was  $\geq 5 \times 10^{12}/\text{cm}^3$ . Several other observations also indicate relatively rapid reaction of Na with the halide. For example, the relatively strong CuCl banded emission which is observed in the discharge through  $(\text{CuCl})_3/\text{Ar}$  mixture is very markedly reduced when Na is admitted into the system. Similarly, the sodium D-line emission which is observed in the discharge through  $(\text{CuCl})_3/\text{Na}/\text{Ar}$  mixtures, is observed to increase in intensity when all of the CuCl deposited on the wall is completely used up.

Although the effort expended to date on this task has been a modest one, the results appear to be rather encouraging. On the basis of the experiments described, it is felt that the production of metal vapor by chemical reaction is feasible and that these studies should be continued, not only with CuCl, but with other metal halides as well.

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